Attachment A

Caramelization

Caramelization is one of the most important types of browning processes in foods, together with Maillard reactions and enzymatic browning. Carmelization leads desirable colour and flavour in bakery's goods, coffee, beverages, beer and peanuts. Undesirable effects of caramelization are for example burned sugar smell and blackening.

Caramelization causes important changes in foods, not only in colour but also in flavour. As no enzymes are involved in the carmelization process, it is a non-enzymatic browning reaction.

Caramelization occure during dry heating and roasting of foods with a high concentration of carbohydrates (sugars).

Simply speaking, caramelization is the process of removal of water from a sugar (such as sucrose or glucose) followed by isomerization and polymerisation steps. In reality the caramelization process is a complex series of chemical reactions, which is still poorly understood.

The process of caramelization starts with the melting of the sugar at high temperatures, followed by foaming (boiling). At this stage saccharose (sugar) decomposes into glucose and fructose. This is followed by a condensation step, in which the individual sugars lose water and react with each other to for example difructose-anhydride. The next step is the isomerization of aldoses to ketoses and further dehydration reactions. The last series of reactions include both fragmentation reactions (flavour production) and polymerization reactions (colour production).

Caramelization starts at relatively high temperatures as compared to the other browning reactions, and depends on the type of sugar. Table 1 below shows the initial caramelization temperatures of some common carbohydrates. This table is based on pure carbohydrates. In foods often several different carbohydrates and other components are present; all these may influence the caramelization temperature as well as the different steps and reactions, and thus the final flavours and colours that are produced.

Table 1 : Initial caramelization temperatures of common carbohydrates

Sugar	Temperature
Fructose	110° C
Galactose	160° C
Glucose	160° C
Maltose	160° C
Saccharose	160° C

The highest rate of the colour development is caused by fructose as caramelization of fructose starts at lower temperature. Baked goods made from honey or fructose syrup thus are generally a bit darker than those made with sugar.

During caramelization several flavour components as well as polymeric caramels are produced. Caramels are complex mixture of various high molecular weight components. They can be classified into three groups:

- Caramelans ($C_{24}H_{36}O_{18}$)
- Caramelens ($C_{36}H_{50}O_{25}$)
- Caramelins ($C_{125}H_{188}O_{80}$)

These polymers are often used as colours in commercial food products, from colas to soy sauce, confectionary and ice-cream. They are labelled as E150.

Commercial caramels are produced directly by heating sugar, or by heating sugar in the presence of co-factors, such as ammonia or sulphite. This results in caramels with different colours or charged caramels. These aspects are very important for the use of different caramels in foods. Caramels used to colour soft drinks should be negatively charged to prevent reaction with phosphates which causes precipitation and loss of colour. On the other hand, caramels used for bakery goods should be positively charged.

The different stages of caramel production all have distinct names, based on the characteristics of the product, see table 2 below. Thread indicates the fact that sugar can be spun into soft or hard threads, ball indicates that sugar easily can be moulded into a proper shape, crack indicates that the sugar will hard after cooling (and cracks when it is broken). Only when colour appears the names refer to caramel.

Table 2 : Stage of caramelization of saccharose (table sugar)

Step		Temperature °C	Description and use	Image
1	Evaporation of water	100	Sugar is melted and impurities rise to the surface;	
2	*Small Thread*	102	No colour; soft cooling; no flavour change. Used in frostings.	
3	*Large Thread*	104	No colour; soft cooling; no flavour change. Used in preserves.	

4	*Small Ball*	110 - 115	No colour; semi-soft cooling; no flavour change. Used in cream candy fillings, Italian meringue, fondants, fudge, and marshmallows;	
5	*Large Ball*	119 - 122	No colour; firm cooling; no flavour change. Used in soft caramels;	
6	*Light Crack*	129	No colour; firm cooling; no flavour change. Used in semi-hard candies.	
7	*Hard Crack*	165 - 166	No colour; hard cooling; no flavour change. Used in butterscotch and hard candies;	
8	*Extra-hard Crack*	168	Slight colour; shatters like glass during cooling; no flavour change. Used in hard candies;	
9	*Light Carmel*	180	Pale amber to golden brown; rich flavour.	
10	*Medium Carmel*	180 - 188	Golden brown to chestnut brown; rich flavour;	
11	*Dark Carmel*	188 - 204	Very dark and bitter; smells burned. Used for colouring, but lack of appropriate sweetness;	
12	Black Jack	210	Also known as "monkey's blood." At this point, the sugar begins to breaks down to pure carbon. Burning flavour.	

Caramelization reactions also result in the formation of flavours. Diacetyl is an important flavour compound, produced during the first stages of caramelization. Diacetyl is mainly responsible for a buttery or butterscotch flavour. Diacetyl is not only produced by caramelization, it can also be produced by bacteria in fermented products, such as beer and yoghurt.

Besides diacetyl hundreds of other flavour compounds are produced for instance furans like hydroxymethylfurfural (HMF) and hydroxyacetylfuran (HAF), furanones such as hydroxydimethylfuranone (HDF), dihydroxydimethylfuranone (DDF) and maltol from disaccharides and hydroxymaltol from monosaccharides.

Hydroxymethylfurfural (HMF) is found in honey, juices, milk but also in cigarettes. Hydroxyacetylfuran (HAF) has a sweet aroma and a low odour threshold. Maltol has a taste reminiscent of freshly baked bread and is used as a flavour enhancer (E636) in breads and cakes.

References:

- Food Chemistry, Dennis D. Miller, 1993
- Larousse Encyclopeadia of food
- http://en.wikipedia.org
- Images : http://www.supertoinette.com/recettes/caramel_to.htm